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Rock Island Arsenal Laboratory

TECHNICAL REPORT

THE USE OF VOLATILE CORROSION INHIBITORS WITH FERROUS AND NONFERROUS METAL FINISHES

By

Robert E. Johnson

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ABSTRACT

Four volatile corrosion inhibitor (VCI) materials were evaluated up to eight years in outdoor, shed, and indoor storage to determine the degree of protection provided to packaged ferrous and nonferrous metal panels with various finishes, and to determine the necessity of providing a well sealed package to reduce the loss of VCI vapors.

The work indicated that there are VCI materials available that will provide satisfactory protection to ferrous metal finishes in extended storage. One of the VCI materials was found to be superior to all other materials evaluated.

It was shown that the VCI materials provided no significant protection to nonferrous finishes, such as cadmium and zinc plate. In general, the VCI materials performed no better than the Kraft paper control, and in certain cases were inferior to the control.

The addition of a supplementary chromate treatment to cadmium and zinc plate increased their protective ability, however, the VCI materials again performed no better than the control.

The addition of an overwrap of MIL-B-121, Grade C barrier material and a coating of VV-S-190 dipcoating wax to the VCI wrapped panels provided the greatest amount of protection to both ferrous and nonferrous finishes.

The extent to which the panels were sealed to confine the VCI vapors was a determining factor in the degree of protection provided. Although some protection was provided by a loosely wrapped panel, the greatest amount was provided by a well sealed package.

RECOMMENDATIONS

1. VCI paper may be utilized on steel, oxide black, and phosphated surfaces where an adequate overwrap can be provided. Care should be exercised in the selection of the VCI paper to be used, however, as one VCI paper proved to be more efficient for long term protection.

2. VCI paper should not be utilized on nonferrous finishes such as cadmium and zinc plate. Should the use of VCI be required where both ferrous and nonferrous metals are present, certain of the VCI papers could be utilized, as they were found to be equal in performance to the Kraft paper control.

THE USE OF VOLATILE CORROSION INHIBITORS WITH FERROUS AND NONFERROUS METAL FINISHES

CONTENTS

THE USE OF VOLATILE CORROSION INHIBITORS WITH FERROUS AND NONFERROUS METAL FINISHES

OBJECT

To determine the degree of protection VCI paper will provide to ferrous and nonferrous metal finishes in outdoor, shed and indoor storage.

To determine the necessity of providing a well sealed package to reduce the loss of VCI vapors.

INTRODUCTION

The Army currently has millions of dollars worth of materiel that has been preserved for indefinite storage. Due to the wide variety of items involved, numerous types of finishes require protection. This includes bare steel surfaces, phosphatized surfaces, black oxide and electrodeposited coatings, such as chrome, cadmium and zinc.

The protective ability of any of the metal finishes is related to the severity of exposure, such as outdoor, shed or indoor storage. The maximum protection can be expected under the mild conditions of indoor storage, while considerably reduced protection can be expected under the severe conditions of outdoor storage.

Information is not available concerning the expected protection of the different finishes in the various types of exposure. Work conducted at this Laboratory will, however, permit a comparison of the protective ability based upon the average life in the 20 percent salt spray test. The average life of the different finishes is as follows:

Protective Finish	Average Salt Spray Life (Hours)
Bare steel	Less than 1/2 hour
Black oxide	1/2
Manganese phosphate	3
Zinc phosphate	8
Chrome plate	30 - 100
Manganese phosphate + oil	48
Zinc phosphate + oil	100
Zinc plate	216
Zinc plate + chromate	480
Cadmium plate	600
Cadmium plate + chromate	3000

These results certainly illustrate the differences in protective ability of the various finishes. It is logical to assume that similar differences would exist in outdoor, shed and indoor storage.

The various finishes are used in numerous applications. These are briefly described as follows:

Black Oxide - Used where tolerances are very critical. It is always used with a coating of MIL-C-14201A, Grade 2.(1)

Manganese and Zinc Phosphate - Used on small arms. Zinc is most desirable, since manganese has less corrosion resistance. Both are used with a coating of MIL-C-14201A, Grade 2(1) or MIL-L-644B.(2)

Chrome Plate - Used in gun barrels and on piston rods. It provides wear resistance.

Cadmium Plate - Used on fasteners, springs, and parts made of brass and bronze. Eliminates galvanic couples. The corrosion products are soluble. Above 350°F it becomes brittle and cracks.

Zinc Plate - Produces insoluble corrosion products. It is never used on threaded components. Above 250°F it becomes brittle and cracks. It decomposes vinyl products.

Cadmium and Zinc Plate + Supplementary Chromate Treatment - Increases the protection of the regular plated finish.

In preparing materiel for long term storage, the ferrous items may be preserved with a light oil or a petrolatum type preservative, dependent upon the severity of exposure. The nonferrous items are given only a coating of oil or solvent dispersed rust preventive, when necessary.

The advent of volatile corrosion inhibitors (VCI) materials provided a new and unique means of preserving materiel for storage. There are certain advantages which make their use very desirable. These are time and convenience. Considerably less time is used in preparing items for storage. The problem of removing a corrosion preventive material is eliminated and the item is ready for immediate use. This represents a savings in time and money.

There are, however, certain factors which prevent or limit the acceptance of VCI materials. The VCI paper is known to have a detrimental affect on cadmium,(3) and areas

of doubt exist concerning other nonferrous metals. In addition to this, the effectiveness of VCI is decreased with loss of the VCI vapors, so that the degree of sealing the package is a critical factor.

In order to provide necessary data concerning the use of VCI materials, it was proposed to investigate the following:

1. To what extent will VCI paper provide protection to ferrous surfaces, conversion coatings and electrodeposited coatings in outdoor, indoor and shed storage.

2. To what extent is it necessary to package in a well sealed package to reduce loss of VCI vapors and subsequent loss of protection.

PROCEDURE AND RESULTS

This investigation covered a period of 8 years and includes phases which were completed within this period. The different phases covered exposure in indoor, shed and outdoor storage and each is discussed separately.

Indoor Storage

This exposure consisted of an unheated warehouse where the ambient temperature ranged anywhere from 0^{o} to 110^{o}F.

The test specimens employed were 2 by 3 by 1/8 inch panels of low carbon steel, conforming to QQ-S-636,[4] and were cleaned in accordance with established cleaning procedures. Five finishes were selected for evaluation and included the following:

1.- Sandblasted

2.- Polished

3.- Oxide Black - Specification MIL-C-13924[5]

4.- Manganese Phosphate - Specification MIL-C-16232B, Type M, Class 3[6]

5.- Zinc Phosphate - Specification MIL-C-16232B, Type Z, Class 3[6]

The sandblasted and polished finishes were obtained using currently acceptable procedures, while the other finishes were prepared in accordance with the applicable specification.

The following VCI materials were included in this investigation:

Material A - VCI paper (35 pound)

Material B - VCI paper (60 pound)

Material C - VCI paper (60 pound)

These three were compared to two controls consisting of a 60 pound neutral Kraft paper and of specimens with no wrap at all.

A number of panels of each of the surface finishes were wrapped in 3-3/4 by 4-1/2 inch pieces of the VCI papers. For control purposes, additional panels were similarly wrapped with the Kraft paper. A rubber band around each wrapped panel held the paper secure. No further wrapping was provided. The wrapped panels were arranged on a rack so that air could circulate freely around them. The bare panel controls were merely placed on a flat surface. The panels were then placed in storage and examined periodically.

Table I indicates the results of indoor exposure and the residual inhibitor content at the time of panel failure. With reference to the exposure results, it is noted that the manganese and zinc phosphate controls, as well as the wrapped panels, were in satisfactory condition after 8 years in storage. The absence of any corrosion on the control panels would indicate only that the VCI papers caused no detrimental effects.

Concerning the sandblasted finish, Material A was found to be inferior to the Kraft paper control. This lack of protection could be due to the hygroscopic nature of the VCI paper. Material B was a considerable improvement, in that it was classed as a borderline failure after 8 years storage. Material C provided the greatest protection, since there was no evidence of any corrosion at the completion of the test.

For polished surfaces, Material A was considered to be no better than the control, while Material B did provide some protection. Material C was superior, as panels were free of corrosion after 8 years storage.

Concerning the oxide black finish, all of the VCI papers provided protection with the most satisfactory performance made by Material C, which was still protecting upon completion of the test.

TABLE I

RESULTS OF INDOOR STORAGE

PANEL FINISH	TYPE OF WRAP				
	BARE PANEL (CONTROL)	KRAFT (CONTROL)	MATERIAL A	MATERIAL B	MATERIAL C
Sandblasted:					
Days to Failure	95	453	177	Borderline Fail at 8 Yrs.	OK at 8 Yrs.
Inhibitor Content (gms/sq ft)	-	-	0.63	None	None
Polished:					
Days to Failure	69	171	177	313	OK at 8 Yrs.
Inhibitor Content (gms/sq ft)	-	-	0.65	None	None
Oxide Black:					
Days to Failure	93	225	400	Fail at 8 Yrs.	OK at 8 Yrs.
Inhibitor Content (gms/sq ft)	-	-	None	None	None
Manganese Phosphate:					
Days to Failure	OK at 8 Yrs.	OK at 8 Yrs.	OK at 8 Yrs.	OK at 8 Yrs.	OK at 8 Yrs.
Inhibitor Content (gms/sq ft)	-	-	None	None	None
Zinc Phosphate:					
Days to Failure	OK at 8 Yrs.	OK at 8 Yrs.	OK at 8 Yrs.	OK at 8 Yrs.	OK at 8 Yrs.
Inhibitor Content (gms/sq ft)	-	-	None	None	None

Concurrent with the periodic examination of the test panels, an effort was made to determine the necessity of providing a well sealed package to reduce the loss of VCI vapors. This involved the analysis of the VCI wrappers for inhibitor content at the time the particular metal finish reached the point of failure. Currently available methods of analysis were employed to determine only the nitrite content. The nitrite analysis was most convenient to conduct, however, no effort was made to analyze for other constituents, since suitable methods were not available.

The minimum nitrite content of the VCI materials at the initiation of the program was as follows:

Material A - 1.0 grams/sq. ft.

Material B - 0.5 grams/sq. ft.

Material C - 2.0 grams/sq. ft.

The residual loading values are indicated in Table I. Since the exposure period covered such a long period of time and the inhibitor had been depleted, few actual values are shown. For Material A, the nitrite had been depleted at the end of 400 days. For Material B, it was 313 days. Although Material C continued to provide protection, several analyses were made on wrappers after three years storage. The results indicated that there was no longer any nitrite present. The continued protection was apparently due to the presence of a film of the chemical on the panel surface.

Shed Storage

This exposure consisted of an enclosed shed physically situated in direct outdoor exposure.

The test panels, surface finishes and VCI materials were the same as those described in the tests conducted for indoor storage.

The results of this exposure are indicated in Table II. It is noted in the table that, with the exception of manganese phosphate, the protection provided by Materials A and B was either no better than the control, or inferior to the control. On the other hand, Material C provided protection to all of the finishes. There did not appear to be any significant difference in the protective ability of Materials A and B.

The residual loading values are also indicated in Table II. Since no effort was made to seal the wrapped panels, it

TABLE II

RESULTS OF SHED STORAGE

PANEL FINISH	TYPE OF WRAP				
	BARE PANEL (CONTROL)	KRAFT (CONTROL)	MATERIAL A	MATERIAL B	MATERIAL C
Sandblasted:					
Days to Failure	3	3	3	3	7
Inhibitor Content (gms/sq ft)	-	-	1.22	0.26	1.65
Polished:					
Days to Failure	4	4	4	4	80
Inhibitor Content (gms/sq ft)	-	-	1.15	0.26	1.31
Oxide Black					
Days to Failure	7	19	15	19	80
Inhibitor Content (gms/sq ft)	-	-	0.87	0.16	1.31
Manganese Phosphate:					
Days to Failure	47	80	115	80	105
Inhibitor Content (gms/sq ft)	-	-	0.18	None	1.18
Zinc Phosphate:					
Days to Failure	95	147	133	119	500
Inhibitor Content (gms/sq ft)	-	-	None	None	None

is noted that the nitrite content steadily decreased with continued exposure. For Material A, the nitrite had been depleted between 115 and 133 days; for Material B, between 19 and 80 days; and for Material C, between 105 and 500 days. For this type of exposure, only the Material C inhibitor provided any consistent or uniform increase in the protection of the various finishes.

Outdoor Storage

This exposure consisted of subjecting wrapped test panels to direct outdoor exposure. The outdoor results will be discussed in two parts. One will cover panels prepared and exposed,as described under the tests for indoor and shed storage. The other will cover tests utilizing additional metal finishes overwrapped with barrier material, with and without a coating of JAN-P-115 wax (now VV-S-190).

In the first part, the test panels, surface finishes and VCI materials were the same as those described in the tests conducted for indoor storage.

The results of this exposure are indicated in Table III. It is noted in the table that, with the exception of manganese phosphate, the protection provided by Material A was only slightly better than or inferior to the control. For the manganese phosphate finish, Material A was superior to the other materials tested. In contrast, Material A was found to be detrimental to the zinc phosphate finish, providing much less protection than the control. Except for being no better than the control on sandblasted finishes, Material B provided protection to all other finishes. Material C again provided protection to all finishes, however, it was not as effective on the manganese phosphate finishes as Material A.

The residual loading values are also indicated in Table III. Due to the severity of the storage conditions, the nitrite content was depleted in a much shorter period of time than was evident in the shed storage. For all intents and purposes, the nitrite in Material A was depleted in 80 days, Material B in 21 days and Material C in 78 days. (The latter value is not shown in the table, since it did not represent a failure time for any of the Material C wrappers.) It should be realized, however, that these values were obtained on panels that were given no overwrap. The use of an overwrap would greatly increase the protective life of the VCI materials.

TABLE III

RESULTS OF OUTDOOR STORAGE

PANEL FINISH	TYPE OF WRAP				
	BARE PANEL (CONTROL)	KRAFT (CONTROL)	MATERIAL A	MATERIAL B	MATERIAL C
Sandblasted:					
Days to Failure	1	2	2	2	6
Inhibitor Content (gms/sq ft)	-	-	0.51	0.14	1.55
Polished:					
Days to Failure	1	2	3	6	63
Inhibitor Content (gms/sq ft)	-	-	0.53	0.05	0.88
Oxide Black:					
Days to Failure	2	2	3	21	27
Inhibitor Content (gms/sq ft)	-	-	0.47	0.02	1.15
Manganese Phosphate:					
Days to Failure	2	50	80	63	63
Inhibitor Content (gms/sq ft)	-	-	0.03	None	0.09
Zinc Phosphate:					
Days to Failure	2	71	14	78	157
Inhibitor Content (gms/sq ft)	-	-	0.18	None	None

In the second part of the outdoor storage program, the five finishes previously discussed were included with the addition of the following:

1 - Chrome plate - Specification QQ-C-320, Class 1, Type I[7]

2 - Cadmium plate - Specification QQ-P-416, Type I, Class 1[8]

3 - Cadmium plate - Specification QQ-P-416, Type II, Class 1[8]

4 - Zinc plate - Specification QQ-Z-325, Type I, Class 1[9]

5 - Zinc plate - Specification QQ-Z-325, Type II, Class 1[9]

The following VCI papers were included in the tests:

Material A - 35 pound

Material B - 60 pound

Material C - 60 pound

Material D - 60 pound

These four were compared to a control consisting of a 60 pound neutral Kraft paper.

A number of panels of each surface finish were wrapped in 3-3/4 by 4-1/2 inch pieces of the VCI papers. For control purposes, additional panels were similarly wrapped with the Kraft paper. All of the panels were then overwrapped with 5-1/4 by 5-3/4 inch pieces of barrier material conforming to Grade C, Type 1 of Specification JAN-B-121 (now MIL-B-121B).[10] A portion of the wrapped panels were then coated with dip-coating wax, conforming to Specification JAN-P-115 (now VV-S-190)[11] and the remaining wrapped panels were left uncoated. All of the panels were then placed in outdoor exposure and periodically examined for evidence of rust or corrosion.

The results of this exposure are indicated in Tables IV and V. Prior to discussing the results, however, it should be mentioned that where a result is shown as OK at a particular number of years, this means that there were not sufficient test panels prepared to continue the test any further, even though the failure time had not been reached.

TABLE IV

RESULTS OF OUTDOOR STORAGE

PANEL FINISH AND METHOD OF WRAP	TYPE OF VCI AND TIME TO FAILURE				
	KRAFT (CONTROL)	MATERIAL A	MATERIAL B	MATERIAL C	MATERIAL D
Sandblasted:					
Grade C only	2 mos.	7-1/2 mos.	9-1/2 mos.	8 mos.	5 mos.
Grade C + Wax	3 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	4 yrs.
Polished:					
Grade C only	2 mos.	15 mos.	18 mos.	12 mos.	5 mos.
Grade C + Wax	3 yrs.	OK @ 4 yrs.	4 yrs.	OK @ 4 yrs.	3 yrs.
Oxide Black:					
Grade C only	2 mos.	3 yrs.	5 yrs.	5-8 yrs.	7-1/2 mos.
Grade C + Wax	3 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	4 yrs.
Manganese Phosphate:					
Grade C only	5-8 yrs.	5 yrs.	5-8 yrs.	5-8 yrs.	5-8 yrs.
Grade C + Wax	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.
Zinc Phosphate:					
Grade C only	5-8 yrs.	5-8 yrs.	5-8 yrs.	5-8 yrs.	5-8 yrs.
Grade C + Wax	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.	OK @ 4 yrs.

TABLE V

RESULTS OF OUTDOOR STORAGE

PANEL FINISH AND METHOD OF WRAP	TYPE OF VCI AND TIME TO FAILURE				
	KRAFT (CONTROL)	MATERIAL A	MATERIAL B	MATERIAL C	MATERIAL D
Chrome Plate:					
Grade C only	6 mos.	6 mos.	6 mos.	3 yrs.	1 yr.
Grade C + Wax	OK @ 2 yrs.	OK @ 2 yrs.	OK @ 2 yrs.	OK @ 2 yrs.	OK @ 2 yrs.
Cadmium Plate:					
Grade C only	6 mos.	5 mos.	6 mos.	8 mos.	5 mos.
Grade C + Wax	2 yrs.	2 yrs.	2 yrs.	2 yrs.	9-1/2 mos.
Cadmium Plate + Supplementary Chromate:					
Grade C only	1 yr.	6 mos.	1 yr.	1 yr.	5 mos.
Grade C + Wax	OK @ 2 yrs.	OK @ 2 yrs.	OK @ 2 yrs.	OK @ 2 yrs.	9-1/2 mos.
Zinc Plate:					
Grade C only	6 mos.	5 mos.	6 mos.	8 mos.	5 mos.
Grade C + Wax	OK @ 2 yrs.	OK @ 2 yrs.	2 yrs.	OK @ 2 yrs.	9-1/2 mos.
Zinc Plate + Supplementary Chromate:					
Grade C only	1 yr.	15 mos.	1 yr.	1 yr.	5 mos.
Grade C + Wax	OK @ 2 yrs.	2 yrs.	OK @ 2 yrs.	OK @ 2 yrs.	9-1/2 mos.

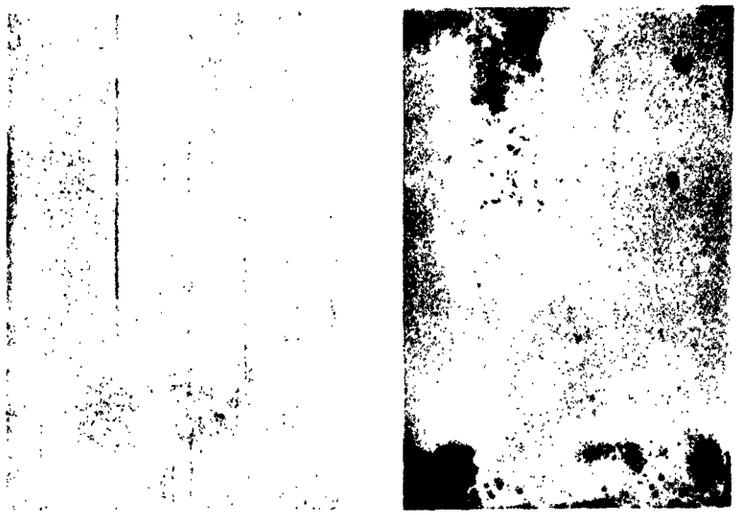
It is noted in Table IV that all of the VCI papers provided protection to the sandblasted finish for both packaging methods. For panels overwrapped in Grade C only, Material B provided the greatest improvement over the control, while Material D provided the least. Figure 1 illustrates the results after 5 months storage where both the control and Material D exhibit rusting, while the other panels are free of rust.

The addition of a wax coating greatly increased the effectiveness of both the control and the VCI papers. With the exception of Material D, which failed after 4 years, the VCI protected panels were satisfactory after 4 years and conceivably would have protected for several more years. These results are illustrated in Figure 2 where the control panel exhibits light rusting, while Material D permitted more extensive rusting.

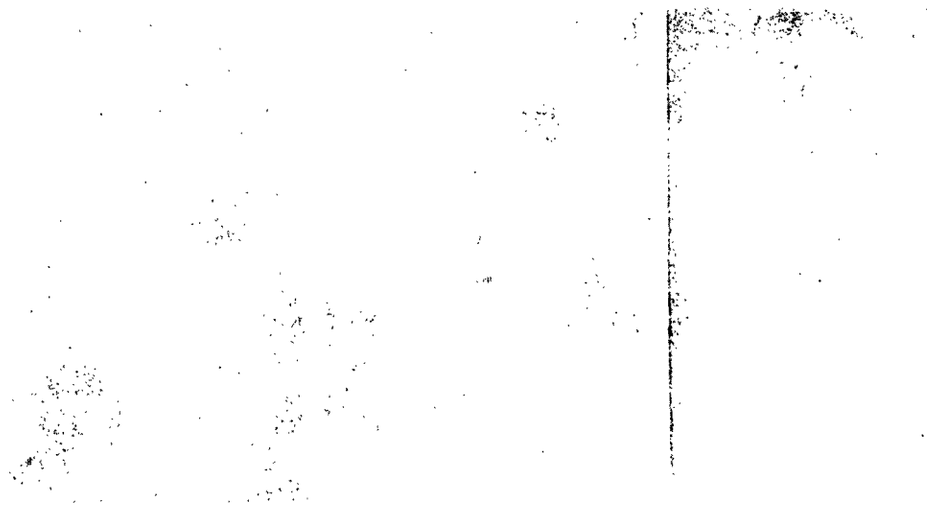
Further referring to Table IV, the polished surfaces were similarly protected by the VCI papers for panels overwrapped in Grade C only. The results after 7-1/2 months storage are shown in Figure 3, where both the control and Material D permitted rusting to develop. With the addition of a wax coating, Materials A, B and C provided protection, while Material D was little improvement over the control. The results, after 4 years storage, are shown in Figure 4, where Materials A and C are still providing protection.

The results for the oxide black panels are also shown in Table IV. All of the VCI materials provided protection for both methods of wrapping the panels where Material D provided only a small degree of protection, the other VCI papers protected from 3 to 8 years.

The application of a wax coating to the packages containing the oxide black finishes greatly increased the protective life. In the case of Materials A, B and C, the number of wax coated packages permitted evaluation only up to 4 years. However, the addition of the wax coating would certainly provide protection beyond the life of the panels packaged in Grade C only. Figure 5 illustrates the condition of the panels after 4 years storage at the time of failure of the control and Material D. The unusual appearance of the panel wrapped in Material C warrants a few words of explanation. The observed condition is not rusting. The darkened areas are stains. The two concentrated areas of stain are probably due to the wrapped package resting against plated nails that were utilized in the exposure racks. There is no plausible explanation as to why this unusual condition occurred with only the Material C paper.



CONTROL MATERIAL D

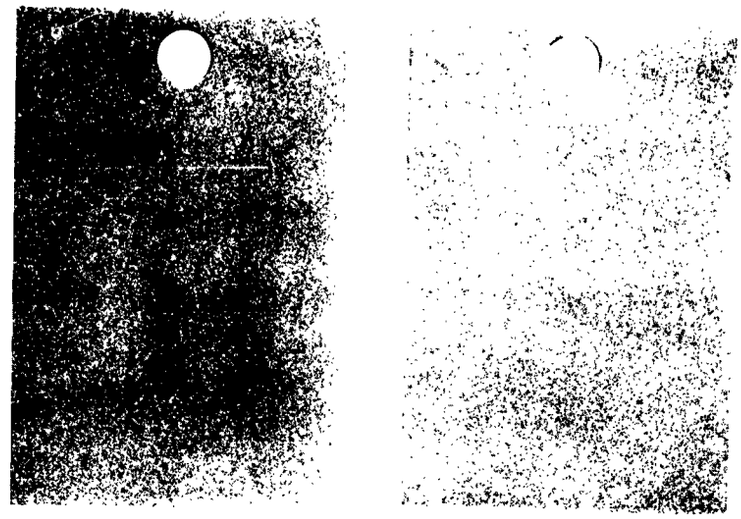


MATERIAL A MATERIAL B MATERIAL C

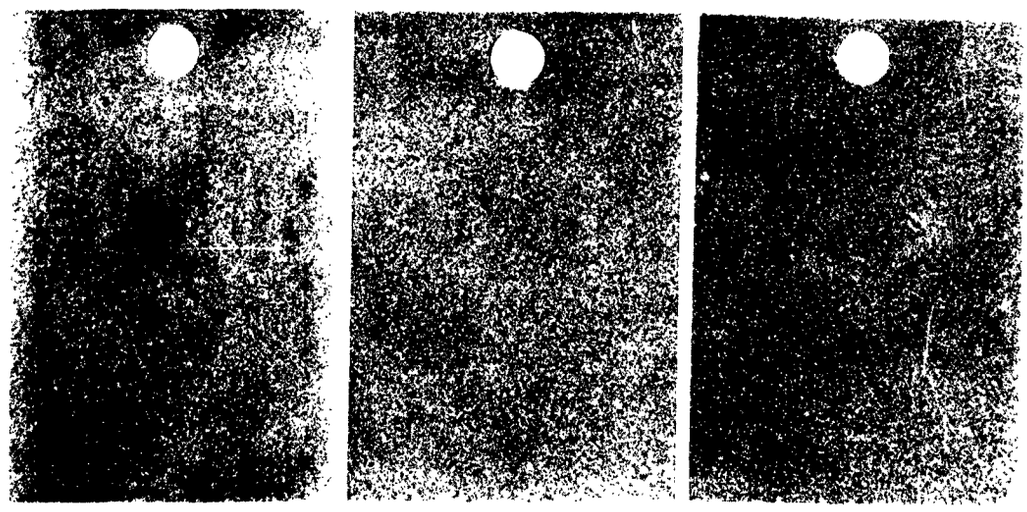
SANDBLASTED PANELS + VCI + GRADE C
AFTER 5 MONTHS OUTDOOR STORAGE

Neg. No. 5622
63-1836

FIGURE 1



CONTROL MATERIAL C

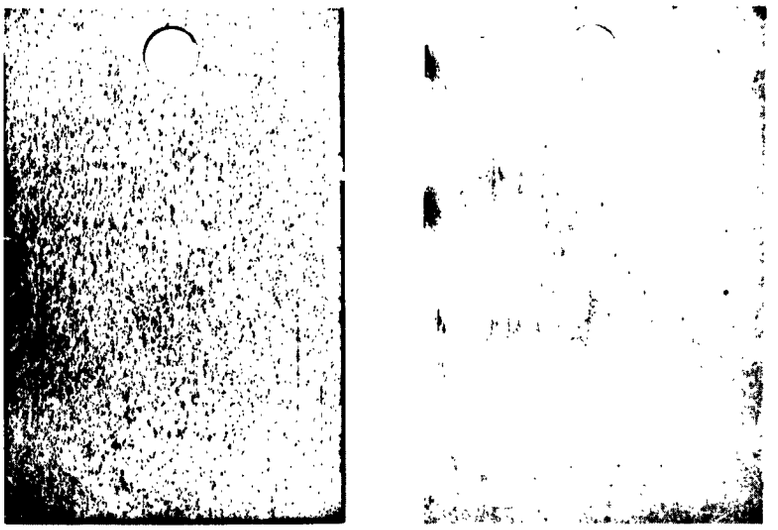


MATERIAL D MATERIAL A MATERIAL B

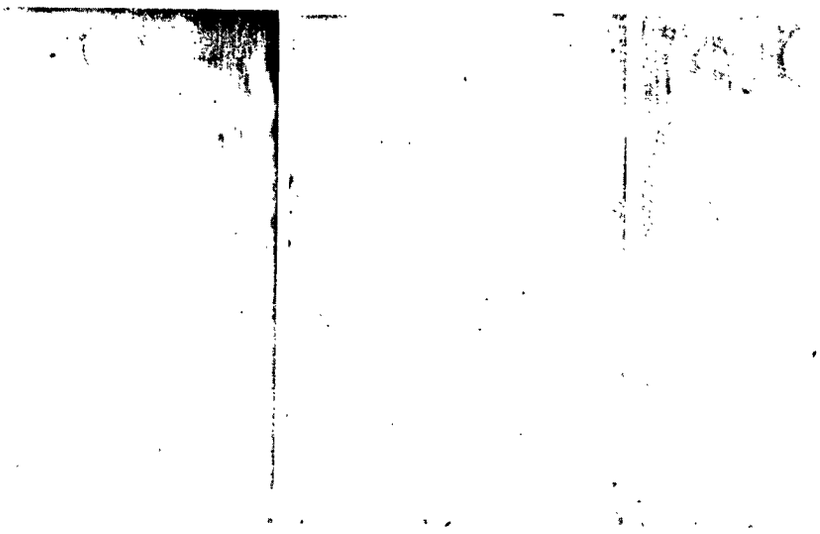
SANDBLASTED TEST PANELS + VCI + GRADE C + WAX
AFTER 4 YEARS OUTDOOR STORAGE

FIGURE 2

Neg. No. 8992
63-1836



CONTROL MATERIAL D

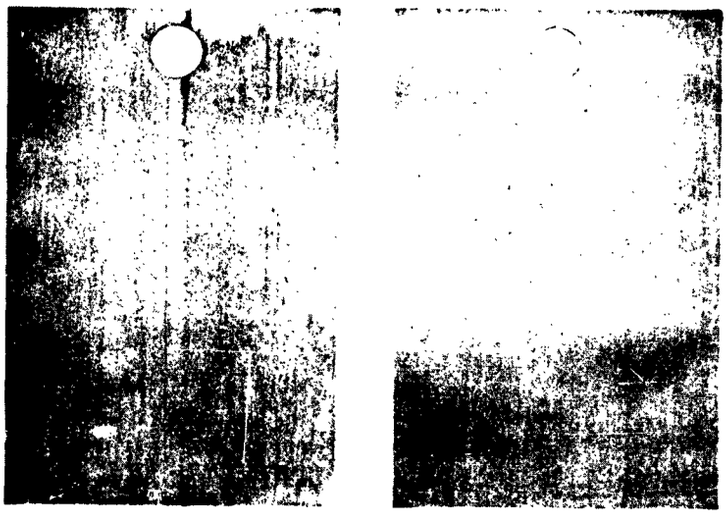


MATERIAL A MATERIAL B MATERIAL C

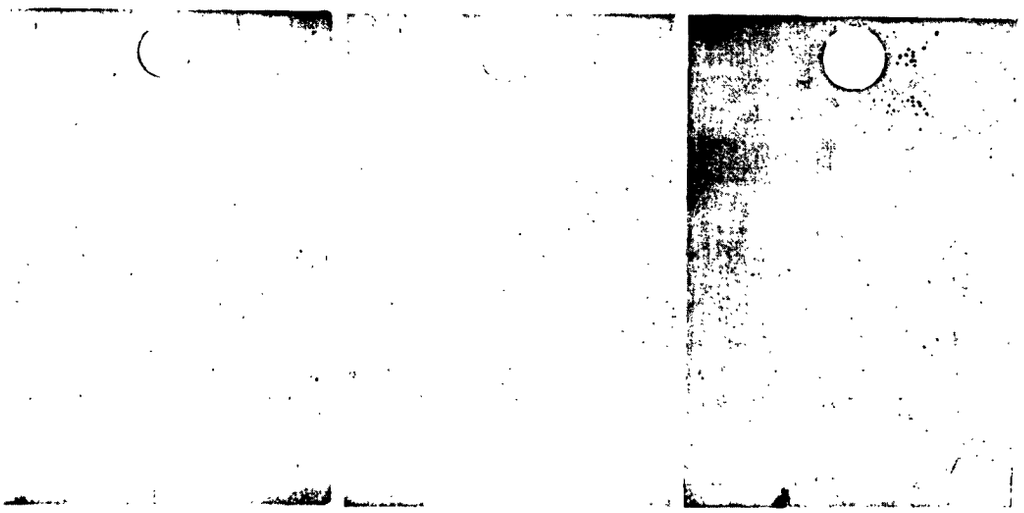
SANDBLASTED PANELS + VCI + GRADE C
AFTER 7-1/2 MONTHS OUTDOOR STORAGE

Neg.No. 5621
63-1836

FIGURE 3



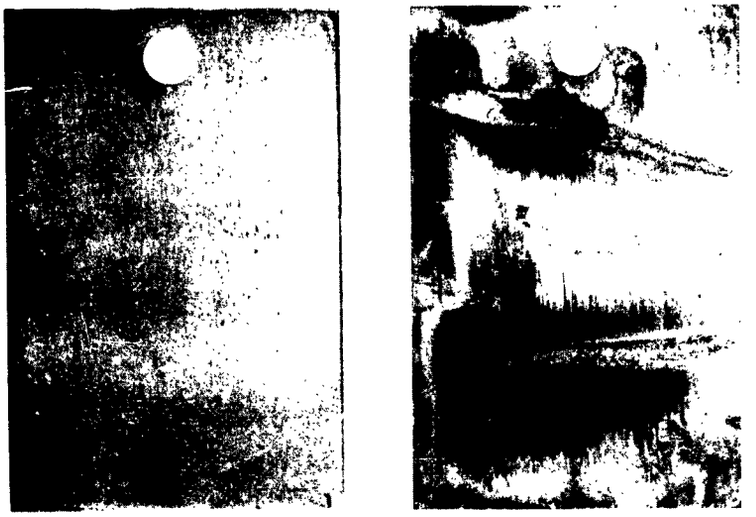
CONTROL MATERIAL C



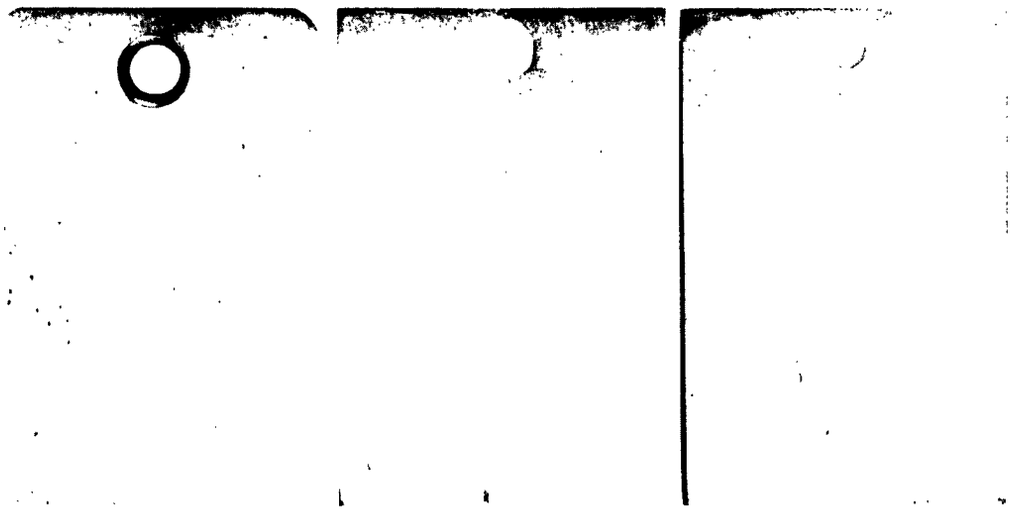
MATERIAL D MATERIAL A MATERIAL B

POLISHED PANELS + VCI + GRADE C + WAX
AFTER 4 YEARS OUTDOOR STORAGE

Neg. No. 8991
63-1836



CONTROL MATERIAL C



MATERIAL D MATERIAL A MATERIAL B

OXIDE BLACK PANELS + VCI + GRADE C + WAX
AFTER 4 YEARS OUTDOOR STORAGE

Neg. No. 8990
63-1836

FIGURE 5

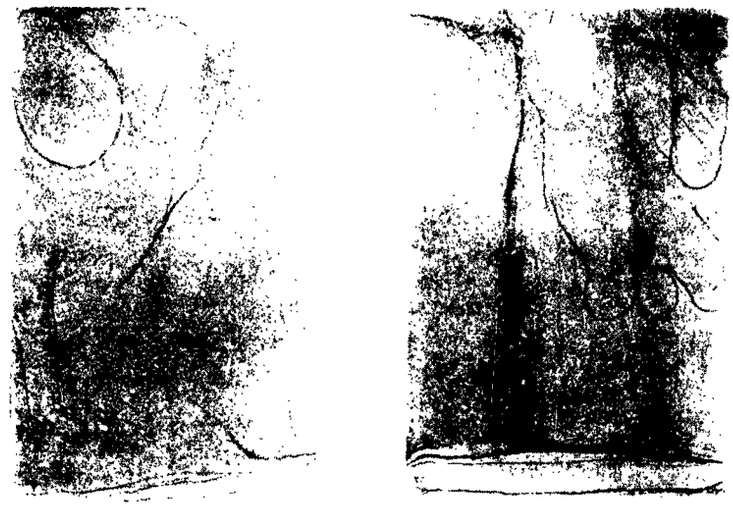
The results for the manganese and zinc phosphated panels are also shown in Table IV. With the exception of Material A on manganese phosphate, which was inferior to the control, none of the VCI papers performed any better than the control. The satisfactory condition of the panels after 4 years storage is shown in Figures 6 and 7. The streaks evident on the panels in Figure 6 are a result of the water rinse after the phosphating process and were evident on the panels when the test was initiated.

At the time this program was terminated, the remaining panels, overwrapped in Grade C only, were examined for extent of corrosion. The condition of panels after 8 years outdoor storage is illustrated in Figures 8 thru 12. The effects of extended storage are noted in the increased severity of the rusting evident. It should be mentioned that some of the panels appear to be more or less corroded than would be expected when compared to other panels in the same figure. This was due to the fact that certain of the Grade C wrappers deteriorated more than others, leaving the panel directly exposed to the atmosphere. This resulted in cases where the VCI wrapped panels were rusted more than the control.

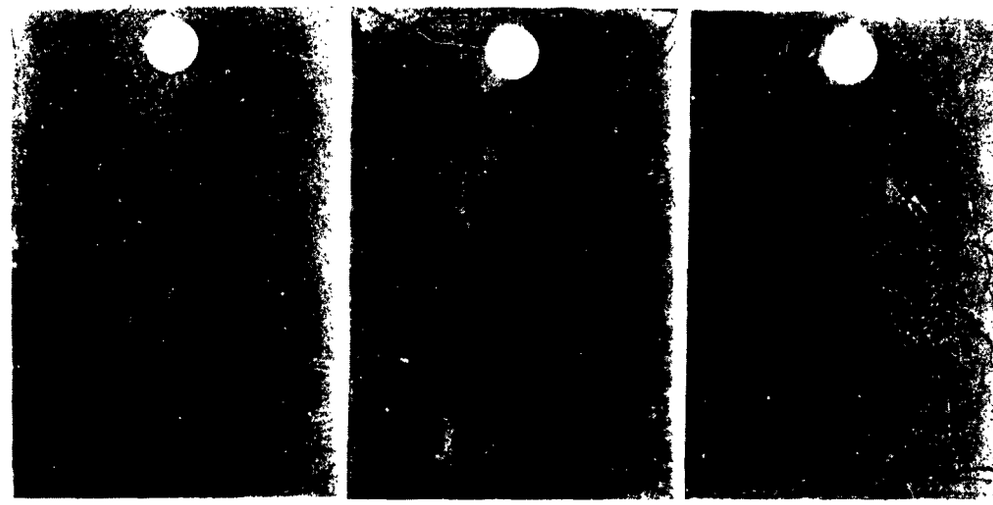
The exposure results for additional nonferrous finishes are indicated in Table V. For the chrome plated finishes, wrapped in Grade C only, Materials C and D provided protection, while Materials A and B were no better than the control. The addition of a wax coating increased the protection of all the papers. All were satisfactory after two years storage and would probably provide protection for several more years. These results are illustrated in Figure 13. The slightly darkened areas on certain of the test panels are stains and should not be construed as corrosion.

Concerning the cadmium plated finishes wrapped in Grade C, only Material C provided any protection. The other VCI papers were either no better than, or inferior to, the control. The application of a wax coating increased the protection provided by all the papers. None of the VCI papers, however, performed any better than the control after 2 years storage. In fact, Material D was inferior to the control. These results are illustrated in Figure 14.

The effect of providing a supplementary chromate treatment to the cadmium plated finish is also shown in Table V. It is noted that Materials B and C were no better than the control, while Materials A and D were inferior to the control. Only the control and Materials B and C provided any significant increase in protection over the regular cadmium



CONTROL MATERIAL C

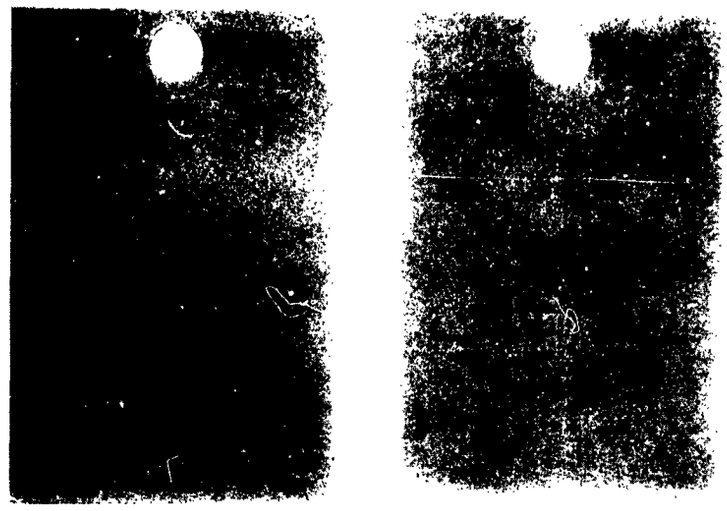


MATERIAL D MATERIAL A MATERIAL B

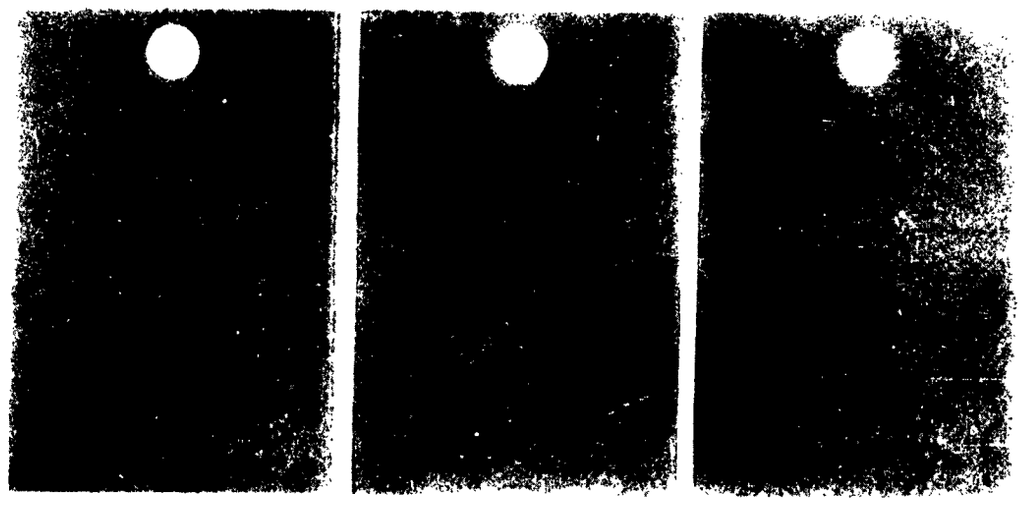
MANGANESE PHOSPHATED PANELS + VCI + GRADE C + WAX
AFTER 4 YEARS OUTDOOR STORAGE

FIGURE 6

Neg. No. 8993
63-1836



CONTROL MATERIAL C

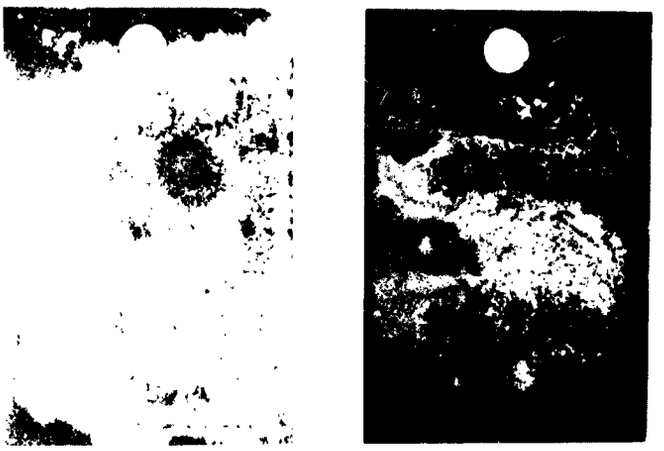


MATERIAL D MATERIAL A MATERIAL B

ZINC PHOSPHATED PANELS + VCI + GRADE C+ WAX
AFTER 4 YEARS OUTDOOR STORAGE

FIGURE 7

Neg. No. 8994
63-1836



CONTROL MATERIAL C

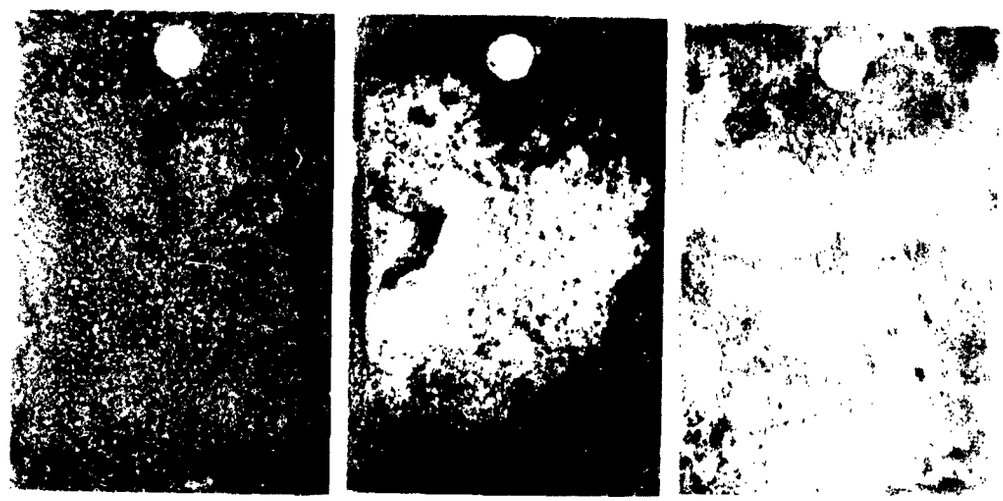
MATERIAL A MATERIAL B MATERIAL D

SANDBLASTED PANELS + VCI + GRADE C
AFTER 8 YEARS OUTDOOR STORAGE

FIGURE 8

Neg. No. 3456
63-1836

CONTROL MATERIAL C

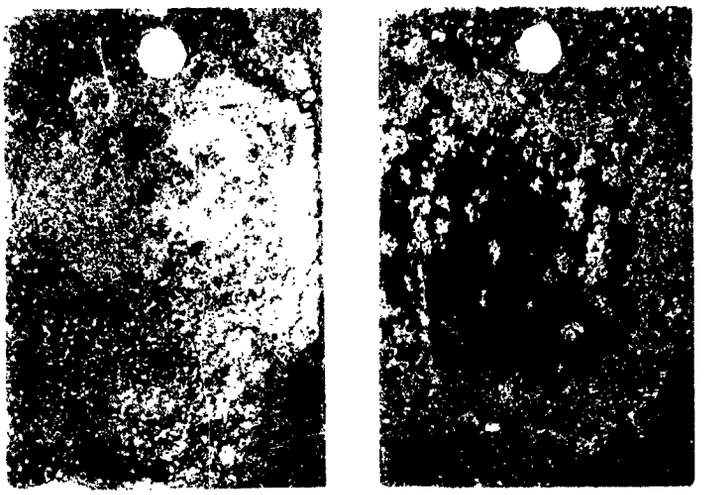


MATERIAL A MATERIAL B MATERIAL D

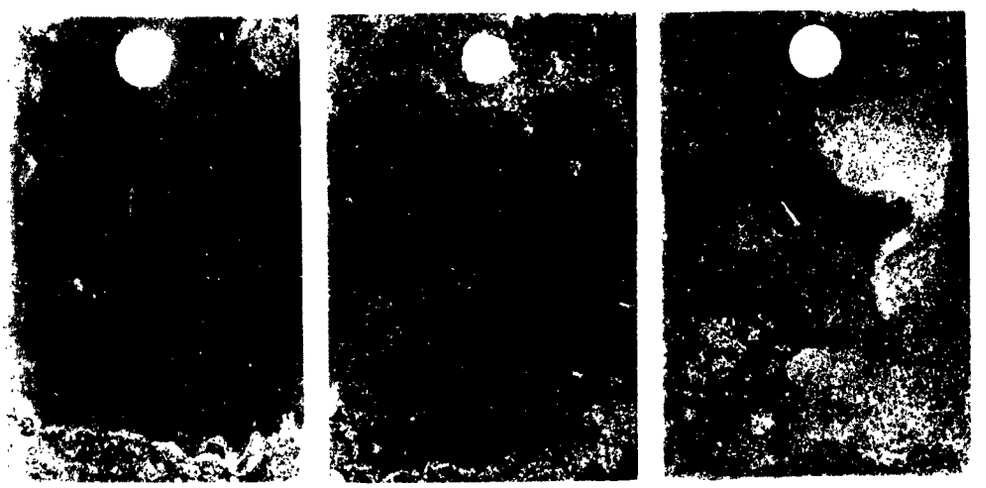
POLISHED PANELS + VCI + GRADE C
AFTER 8 YEARS OUTDOORS STORAGE

FIGURE 9

Neg. No. 3452
63-1836



CONTROL MATERIAL C

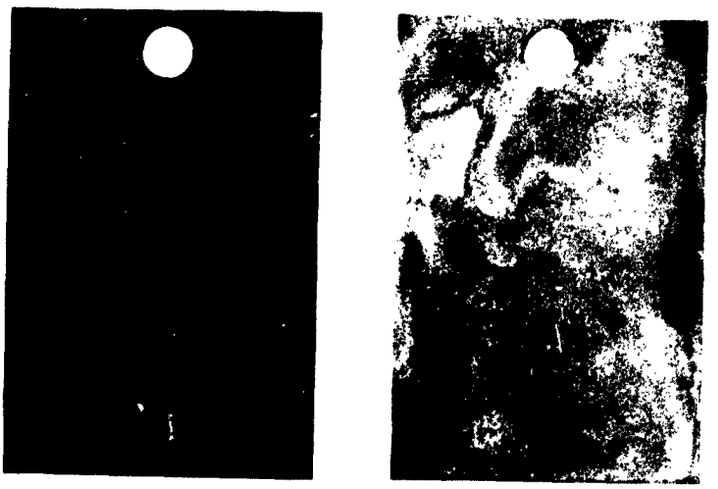


MATERIAL A MATERIAL B MATERIAL D

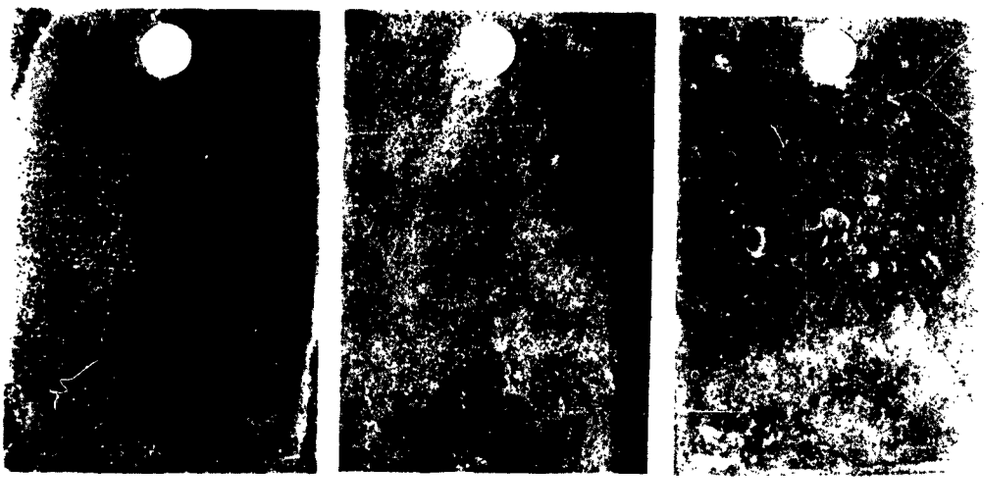
OXIDE BLACK PANELS + VCI + GRADE C
AFTER 8 YEARS OUTDOOR STORAGE

Neg. No. 3455
63-1836

FIGURE 10



CONTROL MATERIAL C



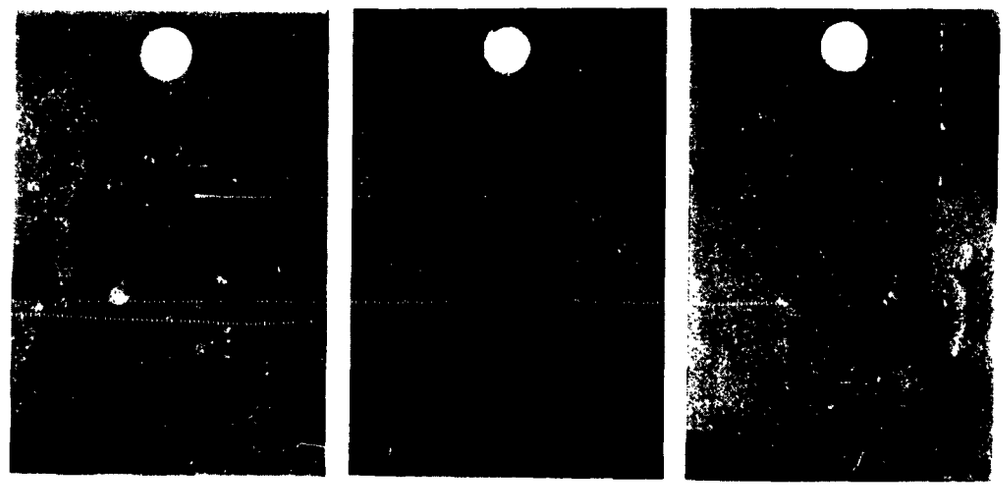
MATERIAL A MATERIAL B MATERIAL D

MANGANESE PHOSPHATED PANELS + VCI + GRADE C
AFTER 8 YEARS OUTDOOR STORAGE

FIGURE 11

Neg. No. 3454
63-1836

CONTROL MATERIAL C

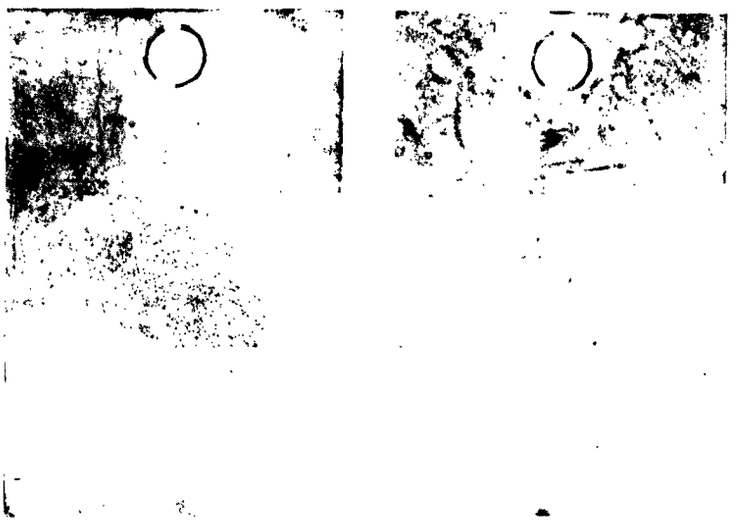


MATERIAL A MATERIAL B MATERIAL D

ZINC PHOSPHATED PANELS + VCI + GRADE C
AFTER 8 YEARS OUTDOOR STORAGE

Neg. No. 3453
63-1836

FIGURE 12



CONTROL MATERIAL C

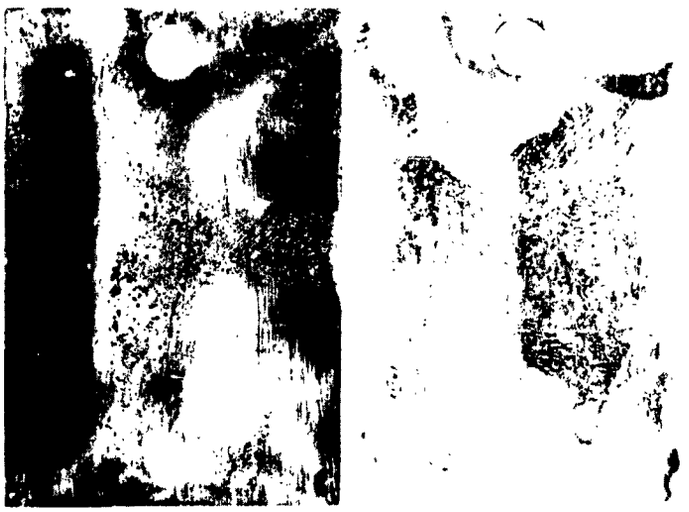
MATERIAL D MATERIAL A MATERIAL B

CHROME PLATED PANELS + VCI + GRADE C + WAX
AFTER 2 YEARS OUTDOOR STORAGE

FIGURE 13

Neg. No. 8398
63-1836

CONTROL MATERIAL C



MATERIAL D MATERIAL A MATERIAL B

CADMIUM PLATED PANELS + VCI + GRADE C + WAX
AFTER 2 YEARS OUTDOOR STORAGE

Neg. No. 8402
63-1836

FIGURE 14

plated finish. A coating of wax increased the protective ability of all the papers. All except Material D were satisfactory after two years exposure. These results are illustrated in Figure 15.

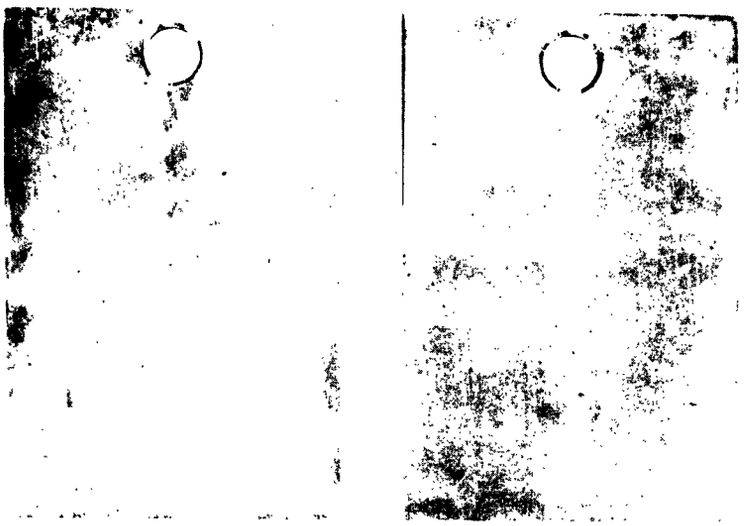
The results of the zinc plated finishes are also shown in Table V. For panels wrapped in Grade C, only Material C provided any protection. The other VCI papers were either no better than, or inferior to, the control. The application of a wax coating increased the protection provided by all the papers. Materials B and D, however, were inferior to the control, while Materials A and C were no better than the control after two years storage. These results are shown in Figure 16.

The results on panels given a supplementary chromate treatment are also shown in Table V. It is noted that Material A provided some protection, while the other VCI papers were either no better than, or inferior to, the control. The control and Materials A, B and C provided an increase in protection over the regular zinc plated finish. The protective ability of all materials was enhanced by the application of a wax coating. After two years exposure, Materials A and D were inferior to the control, while Materials B and C performed similar to the control. These results are illustrated in Figure 17.

At the termination of the program, the panels overwrapped in Grade C only were examined for extent of corrosion. The condition of panels after 6 years outdoor storage is illustrated in Figures 18 thru 22. The effects of extended storage are noted in the increased severity of the corrosion evident. Similar to panels exposed for 8 years (Figures 8 thru 12), there are instances where corrosion on certain panels appears excessive. Here again, this was due to deterioration of the Grade C overwrap, which occurred during extended storage.

DISCUSSION

The performance of the VCI papers under conditions of indoor storage provided varying results. One of the VCI papers, Material C, performed well on all finishes after 8 years storage, while the other VCI papers permitted rusting to occur at an earlier time. All the VCI papers were satisfactory on the phosphated finishes. This should not be considered as providing protection, since the control performed equally as well.

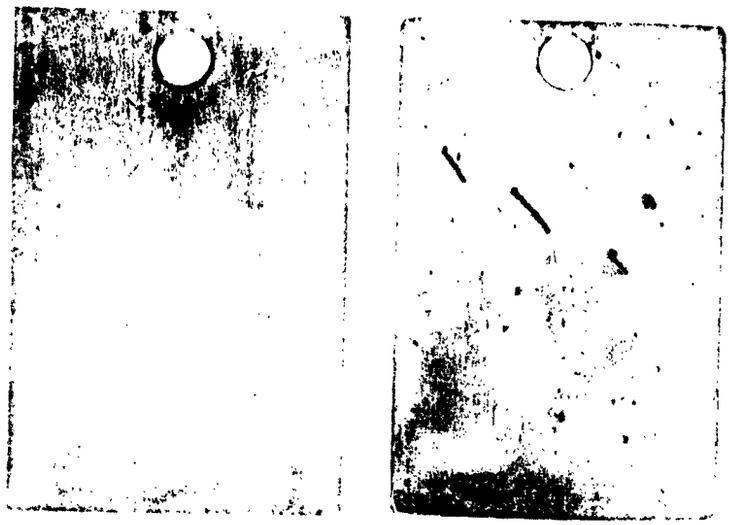


CONTROL MATERIAL C

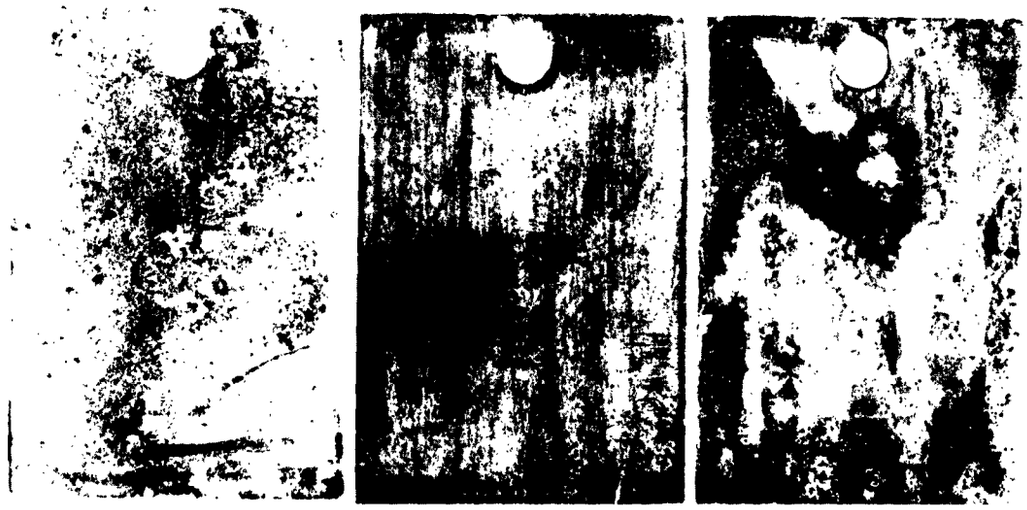
MATERIAL D MATERIAL A MATERIAL B

CADMIUM PLATED PANELS WITH SUPPLEMANTARY CHROMATE + VCI + GRADE C + WAX AFTER 2 YEARS OUTDOOR STORAGE

Neg. No. 8401
63-1836



CONTROL MATERIAL C

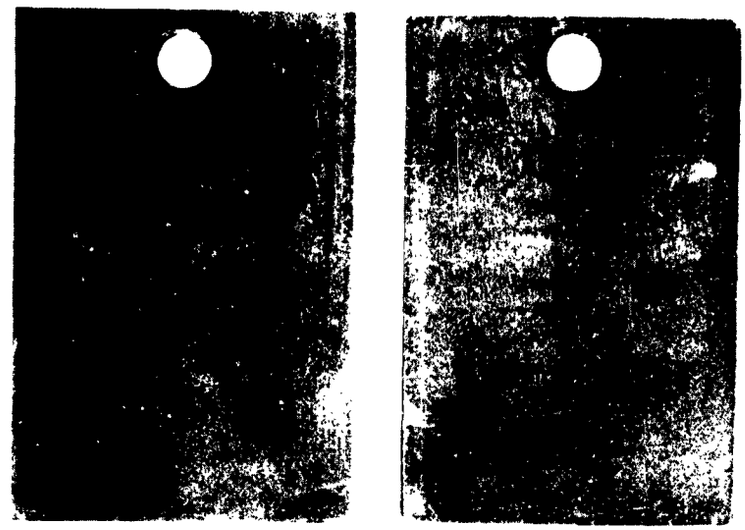


MATERIAL D MATERIAL A MATERIAL B

ZINC PLATED PANELS + VCI + GRADE C + WAX
AFTER 2 YEARS OUTDOOR STORAGE

FIGURE 16

Neg. No. 8400
63-1836



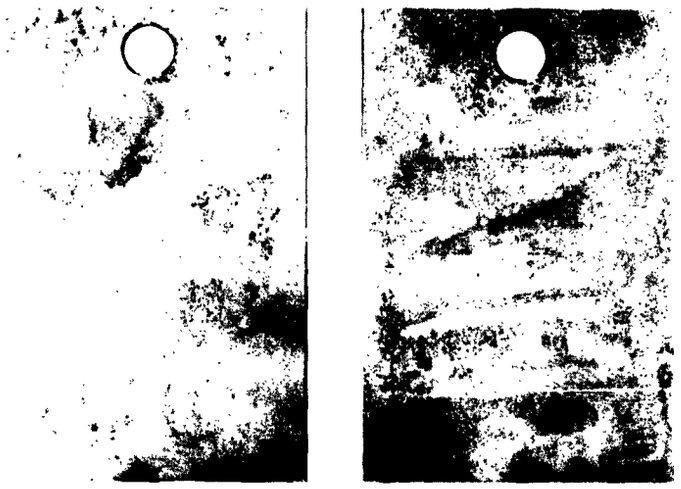
CONTROL MATERIAL C

MATERIAL D MATERIAL A MATERIAL B

ZINC PLATED PANEL WITH SUPPLEMENTARY CHROMATE + VCI + GRADE C + WAX AFTER 2 YEARS OUTDOOR STORAGE

FIGURE 17

Neg. No. 8399
63-1836



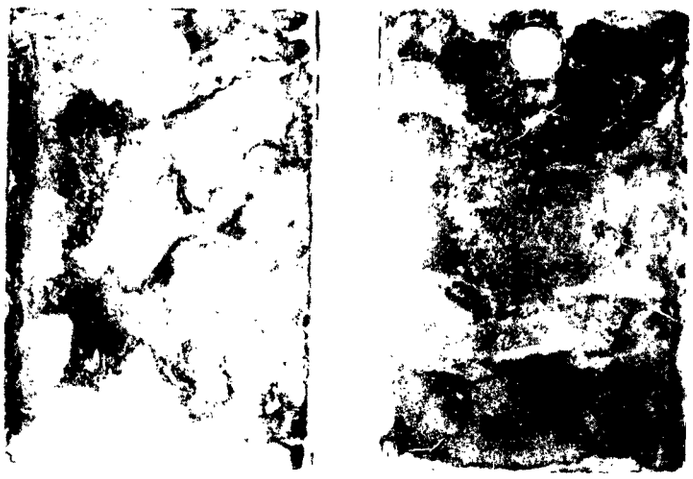
CONTROL MATERIAL C

MATERIAL A MATERIAL B MATERIAL D

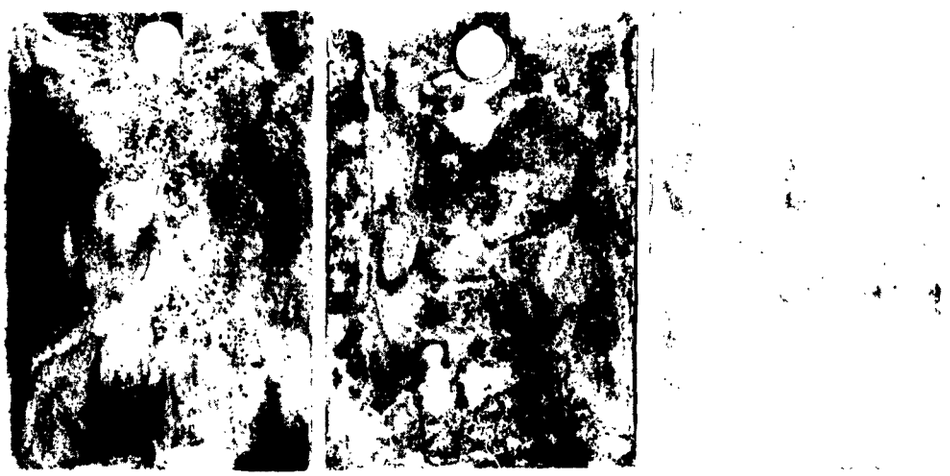
CHROME PLATED PANELS + VCI + GRADE C
AFTER 6 YEARS OUTDOOR STORAGE

FIGURE 18

Neg.No. 3451
63-1836



CONTROL MATERIAL C

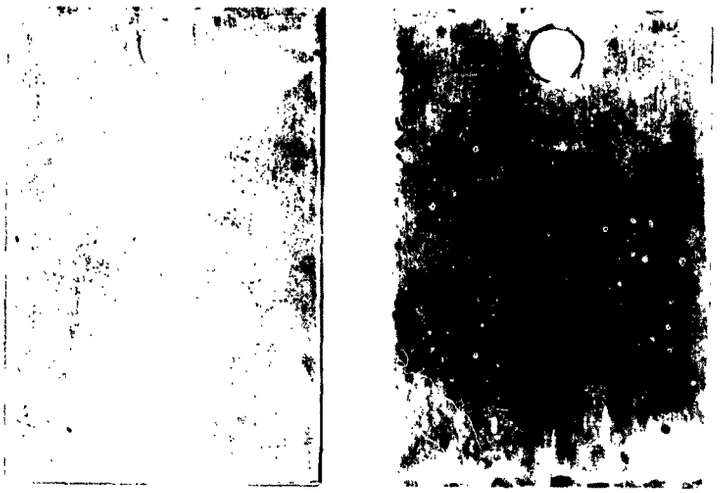


MATERIAL A MATERIAL B MATERIAL D

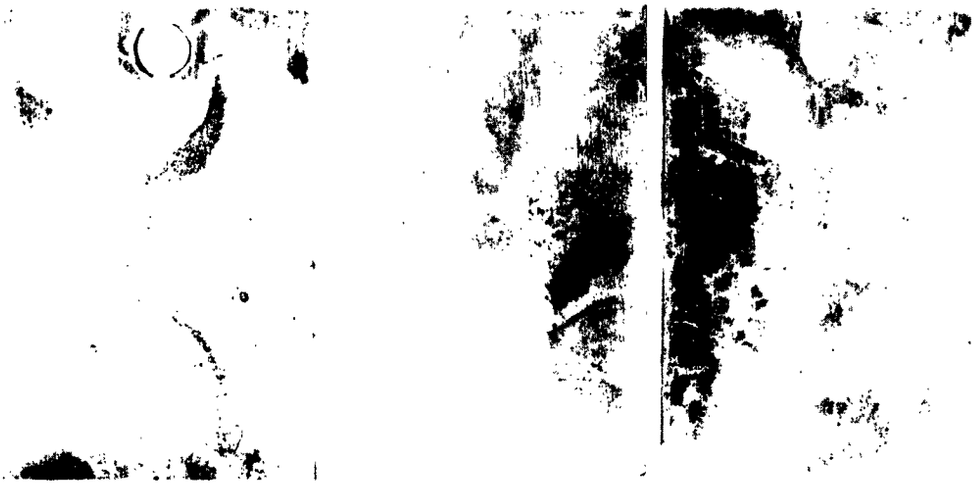
CADMIUM PLATED PANELS + VCI + GRADE C
AFTER 6 YEARS OUTDOOR STORAGE

FIGURE 19

Neg. No. 3450
63-1836



CONTROL MATERIAL C

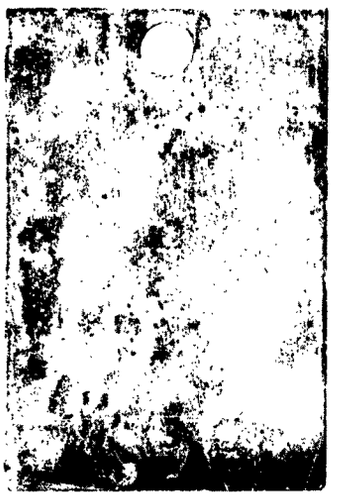


MATERIAL A MATERIAL B MATERIAL D

CADMIUM PLATED PANELS WITH SUPPLEMENTARY CHROMATE + VCI + GRADE C AFTER 6 YEARS OUTDOOR STORAGE

Neg. No. 3449
63-1836

FIGURE 20



CONTROL

MATERIAL C

MATERIAL A

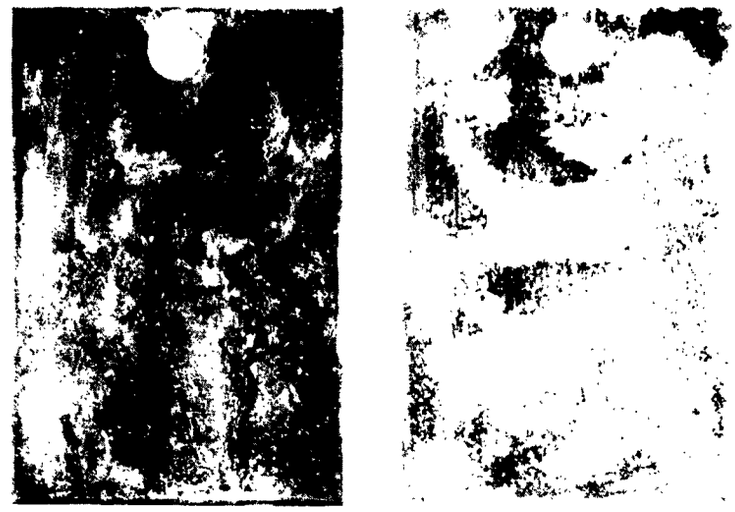
MATERIAL B

MATERIAL D

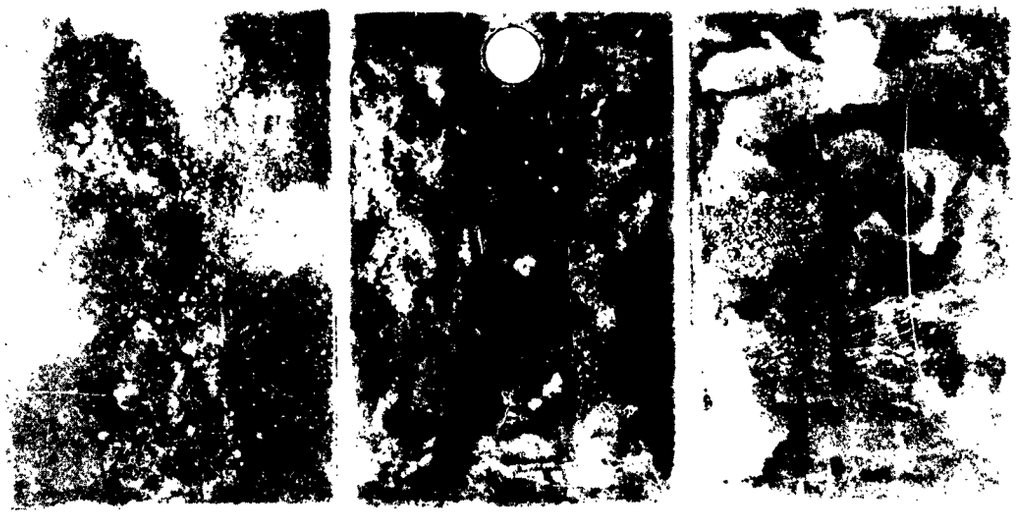
ZINC PLATED PANELS + VCI + GRADE C
AFTER 6 YEARS OUTDOOR STORAGE

Neg. No. 3448
63-1836

FIGURE 21



CONTROL MATERIAL C



MATERIAL A MATERIAL B MATERIAL D

ZINC PLATED PANELS WITH SUPPLEMENTARY CHROMATE + VCI + GRADE C AFTER 6 YEARS OUTDOOR STORAGE

FIGURE 22

Neg. No. 3447
63-1836

Limited information was obtained concerning the residual nitrite available on the papers after exposure. Due to the length of the test, the nitrite had been depleted by the time the particular finish failed and an analysis was conducted. Since the VCI wrapped panels were not sealed in any way, it is readily apparent that the nitrite would eventually be depleted. The continued protection of finishes with Material C was apparently due to the presence of a film of chemical on the panel surface.

As would be expected, considerably less protection was obtained under conditions of shed storage. Similar to indoor storage, Material C performed well on all the finishes. In most cases, Materials A and B did not perform any better than the control.

The residual loading values after shed storage better illustrate the depletion of the nitrite inhibitor. Since the storage conditions were more severe, the nitrite was depleted more rapidly. It should be mentioned that the lower nitrite values evident for Materials A and B were due to the fact that the original nitrite content of the papers was considerably less than for the Material C papers.

The most severe conditions were encountered in outdoor storage. Once again Material C performed well on all the finishes. Although Materials A and B performed well in certain instances, there were cases where the performance was no better than, or even inferior to, the control. It should be kept in mind that these results were obtained on panels wrapped in the VCI paper with no additional wrap provided.

The residual loading values after outdoor storage indicate the more rapid depletion of the nitrite inhibitor. This was expected, however, since the wrapped panels were directly exposed to the elements. For two of the VCI papers, more than 50 percent of the nitrite had been depleted in 2 days.

The addition of an overwrap of Grade C barrier material, with or without a coating of dipcoating wax, greatly increased the protective life of all of the VCI papers in outdoor exposure. For sandblasted, polished and oxide black finishes, Materials A, B and C performed considerably better than the control. Material D, however, did not protect much longer than the control. With the exception of Material A on manganese phosphate, which was inferior to the control, the VCI papers performed similar to the control. Panels wrapped in Grade C only protected for 5 to 8 years and those given a dip in wax were found to be satisfactory after 4 years in

storage. This would indicate that for the phosphated finishes, the VCI papers provided no improvement over the control.

The effects of VCI paper on commonly used nonferrous metals were also investigated and provided interesting results. Chrome plated finishes, given only an overwrap in Grade C, presented no problem as far as Materials C and D were concerned, as both provided protection. Materials A and B however, provided no protection. With the addition of a wax coating, the VCI papers and the control were all satisfactory after 2 years in outdoor storage.

It was shown that the VCI papers provided no significant protection to cadmium and zinc plated finishes. In some cases, the VCI papers were detrimental. This was particularly true with Material D. The addition of a wax coating increased the protective life of all papers, except Material D. It was also revealed that the use of a supplementary chromate treatment extended the protective life of the VCI papers such that most of the panels were satisfactory after 2 years storage. This, however, was no better than the performance of the control. In general, VCI paper was no better than the control, and in some cases produced detrimental effects.

On the basis of the data contained in this report, the following recommendations are made:

1. That VCI paper be utilized on steel, oxide black and phosphated surfaces where an adequate overwrap can be provided. Care should be execised in the selection of the VCI paper to be used, however, as one VCI paper proved to be more efficient for long term protection.

2. That VCI paper not be utilized on nonferrous finishes, such as cadmium and zinc plate. Should circumstances require the use of VCI, certain of the VCI papers could be utilized as they were found to be equal in performance to the control.

In conclusion, it should be mentioned that the data obtained was based upon the performance of VCI papers that were commercially available at the initiation of this program. Improvements in products since that time may well provide an improvement in performance over an extended period of time.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to the Metal Finishes Unit of the Laboratory for providing the necessary test panels and for their assistance in the examination of exposed panels.

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2. Military Specification - MIL-L-644B, "Lubricating Oil, General Purpose, Preservative, Water Displacing, Low Temperature," 4 March 1958.

3. Johnson, Robert E., "The Use of Volatile Corrosion Inhibitors As A Preservative Medium For Long Term Storage of Ordnance Materiel - Addendum VII - Results After Ten Years of Exposure," Rock Island Arsenal Laboratory Report No. 61-544, Project 593-21-062, 9 February 1961.

4. Federal Specification - QQ-S-636, "Steel, Carbon (Low Carbon), Sheets and Strips," 20 June 1941.

5. Military Specification - MIL-C-13924, "Coating, Oxide Black, For Ferrous Metals," 26 December 1956.

6. Military Specification - MIL-C-16232B, "Phosphate Coatings, Heavy, Manganese or Zinc Base, For Ferrous Metals," 9 July 1958.

7. Federal Specification - QQ-C-320, "Chromium Plating, (Electrodeposited)," 11 December 1956.

9. Federal Specification QQ-Z-325, "Zinc Coating, (Electrodeposited), Requirements for," 8 April 1960.

10. Military Specification - MIL-B-121B, "Barrier Material, Greaseproofed, Waterproofed, Flexible," 21 May 1959.

11. Federal Specification - VV-S-190, "Sealing Compound, (Dipcoat)," 26 October 1961.

LIST OF PRIOR REPORTS

R.I.A. LAB NO.	DATE ISSUED	TITLE
51-546	3-12-51	The Use of Volatile Corrosion Inhibitors As A Preservative Medium For the Long Term Storage of Ordnance Materiel.
51-4790	11-16-51	Ibid: Addendum I - Results After Two Years of Exposure.
53-1136	4-7-53	Ibid: Addendum II- Results After Three Years of Exposure.
53-2670	9-22-53	An Evaluation of Analytical Methods for Volatile Corrosion Inhibitors.
53-3712	9-23-53	Volatile Corrosion Inhibitor Bibliography.
53-4921	12-10-53	The Use of Volatile Corrosion Inhibitors As A Preservative Medium for the Long Term Storage of Ordnance Materiel - Addendum III - Results After Four Years of Exposure.
54-3372	10-13-54	An Analytical Method for Urea and An Evaluation of VCI Materials Containing Urea.
55-82	1-7-55	The Use of Volatile Corrosion Inhibitors As A Preservative Medium for the Long Term Storage of Ordnance Materiel - Addendum IV - Results After Five Years of Exposure.
55-3906	10-12-55	An Analytical Method For Dicyclohexylamine.
55-4161	11-3-55	The Use of Volatile Corrosion Inhibitors As a Preservative Medium For the Long Term Storage of Ordnance Materiel - Addendum V - Results After Six Years of Exposure.

LIST OF PRIOR REPORTS

R.I.A. LAB. NO.	DATE ISSUED	TITLE
56-387	2-8-56	Experimental Packaging of Cal. 30, M-1 Carbine in VCI Materials.
56-686	3-8-56	An Evaluation of VCI Materials As Corrosion Inhibitors in Aqueous and Non-Aqueous Solutions.
56-2224	8-3-56	The Effect of Light and Humidity On Volatile Corrosion Inhibitor Papers.
57-2218	9-10-57	Compatibility of VCI With Rubber.
57-2887	12-11-57	Interactions Between Four Volatile Corrosion Inhibitors.
58-1170	5-20-58	Effect of Air Flow on VCI Protection.
58-1591	6-19-58	The Use of Volatile Corrosion Inhibitors As A Preservative Medium For Long Term Storage of Ordnance Materiel - Addendum VI - Results After Eight Years of Exposure.
58-1603	6-19-58	VCI Oils - Properties and Proposed Quality Control Tests.
58-2834	10-16-58	VCI Bibliography and Abstracts.
59-1820	7-6-59	Guide For Practical Preservation With VCI.
59-2929	11-13-59	An Evaluation of Volatile Corrosion Inhibited Oils For the Internal Preservation of Machine Tools In Uncontrolled Storage.
51-544	2-9-61	The Use of Volatile Corrosion Inhibitors As A Preservative Medium For Long Term Storage of Ordnance Materiel - Addendum VII - Results After Ten Years of Exposure.

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THE USE OF VOLATILE CORROSION INHIBITORS WITH FERROUS AND NONFERROUS METAL FINISHES,
by Robert E. Johnson

RIA Lab. Rep. 63-1836, 28 May 63, 47 p. incl. illus. tables, (DA Project No. 1-A-0-24401-A-109, AMC Code No. 5026.11.802) Unclassified Report

Four volatile corrosion inhibitor (VCI) materials were evaluated up to eight years in outdoor, shed and indoor storage to determine the degree of protection provided to packaged ferrous and nonferrous metal panels with various finishes, and to determine the necessity of providing a well sealed package to reduce the loss of VCI vapors.

The work indicated that there are VCI materials available that will provide satisfactory protection to ferrous metal finishes in extended storage. One of the VCI materials was found to be superior to all other materials evaluated.

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It was shown that the VCI materials provided no significant protection to nonferrous finishes, such as cadmium and zinc plate. In general, the VCI materials performed no better than the Kraft paper control, and in certain cases, were inferior to the control.

The addition of a supplementary chromate treatment to cadmium and zinc plate increased their protective ability, however, the VCI materials again performed no better than the control.

The addition of an overwrap of MIL-B-121, Grade C barrier material and a coating of VV-S-190 dipcoating wax to the VCI wrapped panels provided the greatest amount of protection to both ferrous and nonferrous finishes.

The extent to which the panels were sealed to confine the VCI vapors was a determining factor in the degree of protection provided. Although some protection was provided by a loosely wrapped panel, the greatest amount was provided by a well sealed package.

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